



Fig. 4. (A) Methane concentrations in groundwater versus the carbon isotope values of methane. The nonactive and active data depicted in Fig. 3 are subdivided based on the host aquifer to illustrate that the methane concentrations and $\delta^{13}\text{C}$ values increase with proximity to natural-gas well drilling regardless of aquifer formation. Gray areas represent the typical range of thermogenic and biogenic methane taken from Osborn and McIntosh (18). VPDB, Vienna Pee Dee belemnite. (B) Bernard plot (15) of the ratio of methane to higher-chain hydrocarbons versus the $\delta^{13}\text{C}$ of methane. The smaller symbols in grayscale are from published gas-well samples from gas production across the region (16–18). These data generally plot along a trajectory related to reservoir age and thermal maturity (Upper Devonian through Ordovician; see text for additional details). The gas-well data in the orange ovals are from gas wells in our study area in Susquehanna County, Pennsylvania (data from Pennsylvania Department of Environmental Protection). Gray areas represent typical ranges of thermogenic and biogenic methane (data from Osborn and McIntosh, ref. 18).

carbons versus $\delta^{13}\text{C-CH}_4$ (Fig. 4B). Methane concentrations not only increased in proximity to gas wells (Fig. 3), the accompanying $\delta^{13}\text{C-CH}_4$ values also reflected an increasingly thermogenic methane source (Fig. 4A).

Using a Bernard plot (15) for analysis (Fig. 4B), the enriched $\delta^{13}\text{C-CH}_4$ (approximately $> -50\text{‰}$) values accompanied by low ratios of methane to higher-chain hydrocarbons (less than approximately 100) in drinking-water wells also suggest that dissolved gas is more thermogenic at active than at nonactive sites (Fig. 4B). For instance, 12 dissolved-gas samples at active drilling sites fell along a regional gas trajectory that increases with reservoir age and thermal maturity of organic matter, with samples from Susquehanna County, Pennsylvania specifically matching natural-gas geochemistry from local gas wells (Fig. 4B, orange oval). These 12 samples and local natural-gas samples are consistent with gas sourced from thermally mature organic matter of Middle Devonian and older depositional ages often found in Marcellus Shale from approximately 2,000 m below the surface in the northern Appalachian Basin (14–19) (Fig. 4B). In contrast, none of the methane samples from nonactive drilling areas fell upon this trajectory (Fig. 4B); eight dissolved-gas samples in Fig. 4B from active drilling areas and all of the values from nonactive areas may instead be interpreted as mixed biogenic/thermogenic gas (18) or, as Laughrey and Baldassare (17) proposed for their Pennsylvanian gas data (Fig. 4B), the early migration of wet thermogenic gases with low- $\delta^{13}\text{C-CH}_4$ values and high methane-to-higher-chain hydrocarbon ratios. One data point from a nonactive area in New York fell squarely in the parameters of a strictly biogenic source as defined by Schoell (14) (Fig. 4B, upper-left corner).

Carbon isotopes of dissolved inorganic carbon ($\delta^{13}\text{C-DIC} > +10\text{‰}$) and the positive correlation of $\delta^2\text{H}$ of water and $\delta^2\text{H}$ of methane have been used as strong indicators of microbial methane, further constraining the source of methane in shallow groundwater (depth less than 550 m) (18, 20). Our $\delta^{13}\text{C-DIC}$ values were fairly negative and show no association with the $\delta^{13}\text{C-CH}_4$ values (Fig. S3), which is not what would be expected if methanogenesis were occurring locally in the shallow aquifers. Instead, the $\delta^{13}\text{C-DIC}$ values from the shallow aquifers plot within a narrow range typical for shallow recharge waters, with the dissolution of CO_2 produced by respiration as water passes downward through the soil critical zone. Importantly, these values do not indicate extensive microbial methanogenesis or sulfate reduction. The data do suggest gas-phase transport of methane upward to the shallow groundwater zones sampled for this study (<190 m) and dissolution into shallow recharge waters locally. Additionally, there was no positive correlation between the $\delta^2\text{H}$ values of methane and $\delta^2\text{H}$ of water (Fig. S4), indicating that microbial methane derived in this shallow zone is negligible. Overall, the combined gas and formation-water results indicate that thermogenic gas from thermally mature organic matter of Middle Devonian and older depositional ages is the most likely source of the high methane concentrations observed in the shallow water wells from active extraction sites.

A different potential source of shallow groundwater contamination associated with gas drilling and hydraulic fracturing is the introduction of hypersaline formation brines and/or fracturing fluids. The average depth range of drinking-water wells in northeastern Pennsylvania is from 60 to 90 m (12), making the average vertical separation between drinking-water wells and the Marcellus Shale in our study area between approximately 900 and 1,800 m (Fig. 2). The research area, however, is located in tectonically active areas with mapped faults, earthquakes, and lineament features (Fig. 2 and Fig. S1). The Marcellus formation also contains two major sets of joints (21) that could be conduits for directed pressurized fluid flow. Typical fracturing activities in the Marcellus involve the injection of approximately 13–19 million liters of water per well (22) at pressures of up to 69,000 kPa. The majority of this fracturing water typically stays underground and could in principle displace deep formation water upward into shallow aquifers. Such deep formation waters often have high concentrations of total dissolved solids $>250,000$ mg L^{-1} , trace

toxic elements, (18), and naturally occurring radioactive materials, with activities as high as 16,000 picocuries per liter ($1 \text{ pCi L}^{-1} = 0.037 \text{ becquerels per liter}$) for ^{226}Ra compared to a drinking-water standard of 5 pCi L^{-1} for combined ^{226}Ra and ^{226}Ra (23).

We evaluated the hydrochemistry of our 68 drinking-water wells and compared these data to historical data of 124 wells in the Catskill and Lockhaven aquifers (24, 25). We used three types of indicators for potential mixing with brines and/or saline fracturing fluids: (i) major inorganic chemicals; (ii) stable isotope signatures of water ($\delta^{18}\text{O}$, $\delta^2\text{H}$); and (iii) isotopes of dissolved constituents ($\delta^{13}\text{C-DIC}$, $\delta^{11}\text{B}$, and ^{226}Ra). Based on our data (Table 2), we found no evidence for contamination of the shallow wells near active drilling sites from deep brines and/or fracturing fluids. All of the Na^+ , Cl^- , Ca^{2+} , and DIC concentrations in wells from active drilling areas were consistent with the baseline historical data, and none of the shallow wells from active drilling areas had either chloride concentrations $>60 \text{ mg L}^{-1}$ or Na-Ca-Cl compositions that mirrored deeper formation waters (Table 2). Furthermore, the mean isotopic values of $\delta^{18}\text{O}$, $\delta^2\text{H}$, $\delta^{13}\text{C-DIC}$, $\delta^{11}\text{B}$, and ^{226}Ra in active and nonactive areas were indistinguishable. The ^{226}Ra values were consistent with available historical data (25), and the composition of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in the well-water appeared to be of modern meteoric origin for Pennsylvania (26) (Table 2 and Fig. S5). In sum, the geochemical and isotopic features for water we measured in the shallow wells from both active and nonactive areas are consistent with historical data and inconsistent with contamination from mixing Marcellus Shale formation water or saline fracturing fluids (Table 2).

There are at least three possible mechanisms for fluid migration into the shallow drinking-water aquifers that could help explain the increased methane concentrations we observed near gas wells (Fig. 3). The first is physical displacement of gas-rich deep solutions from the target formation. Given the lithostatic and hydrostatic pressures for 1–2 km of overlying geological strata, and our results that appear to rule out the rapid movement of deep brines to near the surface, we believe that this mechanism is unlikely. A second mechanism is leaky gas-well casings (e.g., refs. 27 and 28). Such leaks could occur at hundreds of meters underground, with methane passing laterally and vertically through fracture systems. The third mechanism is that the process of hydraulic fracturing generates new fractures or enlarges existing ones above the target shale formation, increasing the connec-

tivity of the fracture system. The reduced pressure following the fracturing activities could release methane in solution, leading to methane exsolving rapidly from solution (29), allowing methane gas to potentially migrate upward through the fracture system.

Methane migration through the 1- to 2-km-thick geological formations that overlie the Marcellus and Utica shales is less likely as a mechanism for methane contamination than leaky well casings, but might be possible due to both the extensive fracture systems reported for these formations and the many older, uncased wells drilled and abandoned over the last century and a half in Pennsylvania and New York. The hydraulic conductivity in the overlying Catskill and Lockhaven aquifers is controlled by a secondary fracture system (30), with several major faults and lineaments in the research area (Fig. 2 and Fig. S1). Consequently, the high methane concentrations with distinct positive $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ values in the shallow groundwater from active areas could in principle reflect the transport of a deep methane source associated with gas drilling and hydraulic-fracturing activities. In contrast, the low-level methane migration to the surface groundwater aquifers, as observed in the nonactive areas, is likely a natural phenomenon (e.g., ref. 31). Previous studies have shown that naturally occurring methane in shallow aquifers is typically associated with a relatively strong biogenic signature indicated by depleted $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ compositions (32) coupled with high ratios of methane to higher-chain hydrocarbons (33), as we observed in Fig. 4B. Several models have been developed to explain the relatively common phenomenon of rapid vertical transport of gases (Rn , CH_4 , and CO_2) from depth to the surface (e.g., ref. 31), including pressure-driven continuous gas-phase flow through dry or water-saturated fractures and density-driven buoyancy of gas microbubbles in aquifers and water-filled fractures (31). More research is needed across this and other regions to determine the mechanism(s) controlling the higher methane concentrations we observed.

Based on our groundwater results and the litigious nature of shale-gas extraction, we believe that long-term, coordinated sampling and monitoring of industry and private homeowners is needed. Compared to other forms of fossil-fuel extraction, hydraulic fracturing is relatively poorly regulated at the federal level. Fracturing wastes are not regulated as a hazardous waste under the Resource Conservation and Recovery Act, fracturing wells are not covered under the Safe Drinking Water Act, and only recently has the Environmental Protection Agency asked fracturing

Table 2. Comparisons of selected major ions and isotopic results in drinking-water wells from this study to data available on the same formations (Catskill and Lockhaven) in previous studies (24, 25) and to underlying brines throughout the Appalachian Basin (18)

	Active		Nonactive		Previous studies (background)		
	Lockhaven formation N = 8	Catskill formation N = 25	Catskill formation N = 22	Genesee group N = 12	Lockhaven formation (25) N = 45	Catskill formation (24) N = 79	Appalachian brines (18, 23) N = 21
Alkalinity as HCO_3^- , mg L^{-1}	285 ± 36	157 ± 56	127 ± 53	158 ± 56	209 ± 77	133 ± 61	150 ± 171
mM	[4.7 ± 0.6]	[2.6 ± 0.9]	[2.1 ± 0.9]	[2.6 ± 0.9]	[3.4 ± 1.3]	[2.2 ± 1.0]	[2.5 ± 2.8]
Sodium, mg L^{-1}	87 ± 22	23 ± 30	17 ± 25	29 ± 23	100 ± 312	21 ± 37	33,000 ± 11,000
Chloride, mg L^{-1}	25 ± 17	11 ± 12	17 ± 40	9 ± 19	132 ± 550	13 ± 42	92,000 ± 32,000
Calcium, mg L^{-1}	22 ± 12	31 ± 13	27 ± 9	26 ± 5	49 ± 39	29 ± 11	16,000 ± 7,000
Boron, $\mu\text{g L}^{-1}$	412 ± 156	93 ± 167	42 ± 93	200 ± 130	NA	NA	3,700 ± 3,500
$\delta^{11}\text{B}$ ‰	27 ± 4	22 ± 6	23 ± 6	26 ± 6	NA	NA	39 ± 6
^{226}Ra , pCi L^{-1}	0.24 ± 0.2	0.16 ± 0.15	0.17 ± 0.14	0.2 ± 0.15	0.56 ± 0.74	NA	6,600 ± 5,600
$\delta^2\text{H}$, ‰, VSMOW	−66 ± 5	−64 ± 3	−68 ± 6	−76 ± 5	NA	NA	−41 ± 6
$\delta^{18}\text{O}$, ‰, VSMOW	−10 ± 1	−10 ± 0.5	−11 ± 1	−12 ± 1	NA	NA	−5 ± 1

Some data for the active Genesee Group and nonactive Lockhaven Formation are not included because of insufficient sample sizes (NA). Values represent means ± 1 standard deviation. NA, not available.

N values for $\delta^{11}\text{B}$ ‰ analysis are 8, 10, 3, 6, and 5 for active Lockhaven, active Catskill, nonactive Genesee, nonactive Catskill, and brine, respectively. N values for ^{226}Ra are 6, 7, 3, 10, 5, and 13 for active Lockhaven, active Catskill, nonactive Genesee, nonactive Catskill, background Lockhaven, and brine, respectively. $\delta^{11}\text{B}$ ‰ normalized to National Institute of Standards and Technology Standard Reference Material 951. $\delta^2\text{H}$ and $\delta^{18}\text{O}$ normalized to Vienna Standard Mean Ocean Water (VSMOW).

firms to voluntarily report a list of the constituents in the fracturing fluids based on the Emergency Planning and Community Right-to-Know Act. More research is also needed on the mechanism of methane contamination, the potential health consequences of methane, and establishment of baseline methane data in other locations. We believe that systematic and independent data on groundwater quality, including dissolved-gas concentrations and isotopic compositions, should be collected before drilling operations begin in a region, as is already done in some states. Ideally, these data should be made available for public analysis, recognizing the privacy concerns that accompany this issue. Such baseline data would improve environmental safety, scientific knowledge, and public confidence. Similarly, long-term monitoring of groundwater and surface methane emissions during and after extraction would clarify the extent of problems and help identify the mechanisms behind them. Greater stewardship, knowledge, and—possibly—regulation are needed to ensure the sustainable future of shale-gas extraction.

Methods

A total of 68 drinking-water samples were collected in Pennsylvania and New York from bedrock aquifers (Lockhaven, 8; Catskill, 47; and Genesee, 13) that overlie the Marcellus or Utica shale formations (Fig. S1). Wells were purged to remove stagnant water, then monitored for pH, electrical conductance, and temperature until stable values were recorded. Samples were collected “upstream” of any treatment systems, as close to the water well as possible, and preserved in accordance with procedures detailed in *SI Methods*. Dissolved-gas samples were analyzed at Isotech Laboratories and water chemical and isotope (O, H, B, C, Ra) compositions were measured at Duke University (see *SI Methods* for analytical details).

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